

5.1.2. RITS CONTINUOUS GAS CHROMATOGRAPH SYSTEMS

During scheduled maintenance trips to the field sites, calibration tank regulator heaters and automatic shut-off solenoid valves were installed. The regulator heaters operate at 60°C and reduce contamination buildup. The solenoid valves are in-line between the two calibration tank regulators and the stream select valve. If a power outage occurs, the solenoid valves close preventing the possible loss of valuable calibration gases.

Electron capture detectors (ECDs) at BRW, NWR, and SMO had to be replaced during 1993. In all cases the channel that measures CFC-11, CFC-113, CH_3CCl_3 , and CCl_4 was the one that had baseline frequency gradually increase from a nominal 100 Hz to well over 1000 Hz. The method of cleaning a detector by flowing H_2 through it at normal operating temperature for 24 hours or more did not improve the background frequency.

Calibration cylinder gases at the field sites typically last about 1.5 years. The ratios of the chromatogram areas for all components in the two calibration tanks are monitored for possible drift. When a calibration cylinder's pressure falls below 1.3 MPa it is replaced. The new tank components' mixing ratios were determined with a precision better than 0.5%. For a chemical like N_2O , whose growth rate in the atmosphere is small being similar to the calibration precision, step jumps can occur in the data when calibration gases are changed. A technique to counteract this problem and also attempt to detect drift in the working standards was instituted in 1993. Two well-calibrated gas standards (round robins), one at ambient and the other at ~10% below ambient mixing ratios, were taken to the field sites over a period of a month and analyzed in place of outside air for 2 days. This intercalibration documented working standard mixing ratios over a span of a few weeks at all of the sites except SPO. GC linearity and precision were also determined. By continuing this procedure quarterly, problems associated with standards' drift and instrument vagaries should be minimized. Some adjustments in the data base will probably be required as this method becomes routine and attempts are made to back correct the data based on better defined instrument calibration curves.

Monthly mean data for CFC-11 are pictured in Figure 5.3. The marked decrease in growth rate is obvious and comparable to that determined from the longer flask record. Likewise, CFC-12 data are shown in Figure 5.4 and correlate well with the flask mixing ratios. The data for N_2O (Figure 5.5) were adjusted because of the round robin intercalibrations. These data are preliminary and may require further adjustment as the intercalibrations continue. NWR data were corrected for the period when the Nafion drier was not installed. This removed or reduced the annual cycle seen in previously published results.

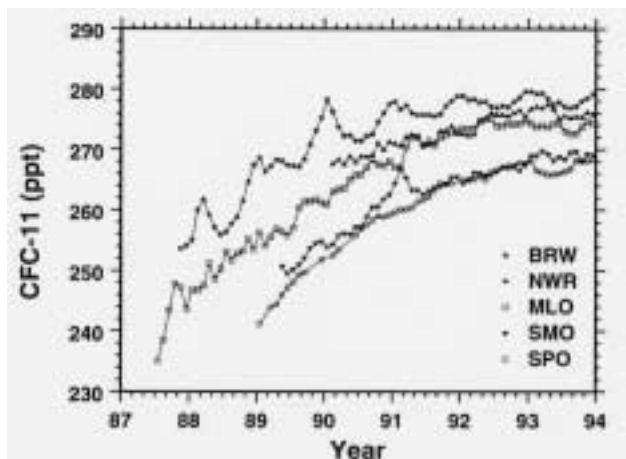


Fig. 5.3. Monthly average CFC-11 mixing ratios in ppt from the in situ GCs.

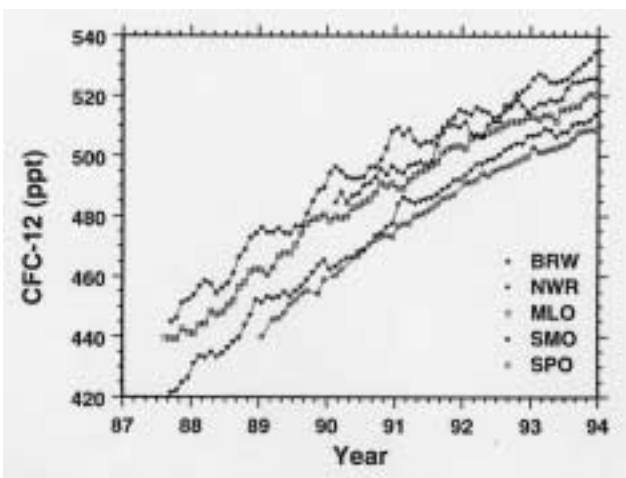


Fig. 5.4. Monthly average CFC-12 mixing ratios in ppt from the in situ GCs.

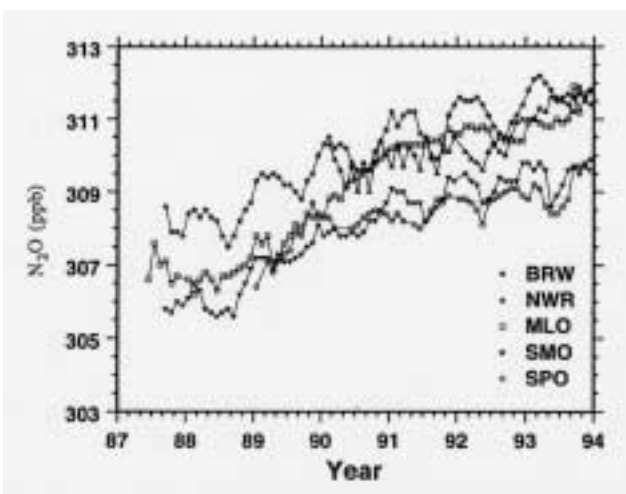


Fig. 5.5. Monthly average N_2O mixing ratios in ppb from the in situ GCs. New calibration and water vapor corrections were applied.